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Variation with Polyol Molecular Weight of Structures at the Surface and the Substrate Interface, and Bulk of Polyurethane Films

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Beamline(s): X14A

Introduction: The phase separation of soft and hard segment toward the air-polyurethane surface and polymer-substrate interface was examined. This was conducted by investigation of the structural differences between the air surface, interface and bulk films as a function of polyol molecular weight.

Methods and Materials: Polyurethane films were solution cast onto Al film substrates. The polyurethane films investigated were consisted of polyether polyol soft segments and diphenylmethane-4:4'-diisocyanate (MDI) and butanediol (BDO) hard segments. The structural differences at the polymer surface, the polymer/Al interface, and the bulk polymer were examined using grazing and wide angle X-ray scattering. The results were confirmed by the optical micrographs for the polymer film surfaces and the peeled polymer interfaces.

Results: The air polymer surface has a quite different structure from the bulk film and the polymer/Al interface. Tape-peeled Al surfaces showed the presence of type II MDI/BDO crystallites in the polymer film residues, while co-existence of type I and II crystals (Table 1) appeared at air surface and in the bulk polymer (Tables 1 and 2). Crystallization of soft segments took place in films with a polyol molecular weight of 1000 g/mol. In addition, formation and/or segregation of soft segment crystallites at the polymer/Al interface resulted in a greater number of polymer residues after peeling. The interpretations of the grazing angle scans for the peeled polymer surfaces and the air surfaces were corroborated by the optical microscopy data; the surface spherulites, consisting of soft segment crystallites, showed up at the surfaces of polyurethane films with polyol molecular weights of over 1000 g/mol. From the interplanar spacings, the interaction of the polymer with the Al surface resulted in local ordering and strained chain alignments. It was determined that polyurethane film has three layers: air-polymer surface, bulk, and substrate-facing polymer layer.

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References:

[1] R.M. Briber and E.L. Thomas, *J. Macromol. Sci.-Phys.*, **B22(4)**, 509-528 (1983).

Table 1. Interplanar spacings (Å) of reflections for type I and II crystals of MDI/BDO crystallites [1].

Type I	7.70, 5.01, 3.89, 3.53, 3.33
Type II	8.60, 4.94, 4.61, 4.45, 4.16, 3.81, 3.51, 2.58, 2.49, 2.08, 1.93, 1.73, 1.61, 1.43, 1.26, 1.00

Table 2. Interplanar spacings (Å) for polyurethane films of various polyol molecular weights, from grazing and wide angle X-ray scatterings. *H* indicates hard segments and *S* soft segment.

Molecular weight	Air surface	Bulk film	Peeled polymer interface	Film residues
MDI/BDO only	5.00, 4.63, 4.15, 3.28 (H)	11.33, 5.54, 4.62, 4.23, 3.86, 3.30, 2.78 (H)	5.11, 4.73, 4.21, 3.69, 3.46, 3.32 (H)	4.58, 4.21 (H)
650	No peaks	11.33, 6.00, 5.61, 4.62, 4.23, 3.86, 3.46, 3.30, 2.78 (H)	6.02, 5.04, 4.65, 4.21, 3.45 (H)	6.04, 4.21, 3.45 (H)
1000	4.50 (S) 4.21 (H)	3.63 (S) 11.33, 4.97, 4.62, 4.27, 3.87, 3.30 (H)	8.25, 4.21, 3.45 (H)	6.04, 4.91, 4.21, 3.46 (H)
1400	4.42, 3.64 (S) 4.21 (H)	3.65 (S) 11.33, 4.94, 4.62, 4.27, 3.87, 3.30 (H)	4.49, 3.69 (S) 6.02, 4.73, 4.22, 3.45 (H)	4.49, 3.69 (S) 4.15, 3.45 (H)
2000	4.42, 3.64 (S) 4.67, 4.15, 4.01 (H)	4.48, 3.65 (S) 11.33, 4.93, 4.67, 4.23, 3.30 (H)	No peeling	No peeling
2900	4.41, 3.64 (S) 4.65, 4.18 (H)	4.48, 3.65 (S) 5.98, 4.93, 4.67, 4.19, 3.42, 3.30 (H)	No peeling	No peeling